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Impact of Crystalline Orientation on the Switching Field in Barium Titanate Using Piezoresponse Force Spectroscopy

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ABSTRACT

Understanding crystal orientation at the ferroelectric domain level, using a non destructive technique, is crucial for the design and characterization of nano-scale devices. In this study, piezoresponse force spectroscopy (PFS) is used to identify ferroelectric domain orientation. The impact of crystal orientation on the switching field of ferroelectric BaTiO₃ is also investigated at the domain level. The preferential domain orientations for BaTiO₃ thin films prepared by pulsed laser deposition (PLD) in this study are [001], [101] and [111]. They have been mapped onto PFS spectra to show three corresponding switching fields of 460, 330 and 120 kV/cm respectively. In addition, the electric field at which the enhanced piezoresponse occurs was found to vary, due to a phase change. The polarization reversal occurs via a 2-step process (rotation and switching) for [101] and [111] orientations. The piezoresponse enhancement is absent for the [001] (pure switching) domains. The results demonstrate that an electric field induced phase change causes the [101] and [111] domains to reverse polarization at a lower field than the [001] domain.

INTRODUCTION

The multitude of applications that piezoresponse force microscopy (PFM) can offer have revolutionized nano-scale domain studies of ferroelectric materials recently [1]. Tip induced polarization switching has greatly improved the resolution of domain imaging and spectroscopy. Piezoresponse force spectroscopy (PFS) is a static spectroscopic mode which is based on the detection of local inverse piezoelectric deformations of domains by an external electric field induced by an atomic force microscopy (AFM) tip. A detailed description of PFS technique is given elsewhere [2].

Previous experimental studies have shown that ferroelectric materials like BaTiO₃ exhibit an enhanced piezoresponse in certain directions under the application of an external electric field [3][4]. Polarization rotation from the tetragonal to rhombohedral phase and vice versa through intermediate monoclinic phase is found to be the reason for this extraordinary piezoresponse [5]. The application of an electric field which is not in alignment with the c-axis of the crystal would result in the phase transformation causing a variation in strain, which leads to an extraordinary piezoresponse.

First principles molecular dynamics simulations have shown that, in BaTiO₃, the phase transition through the monoclinic phase facilitates polarization reversal at a low electric field [6]. It was also shown that, when the polarization is parallel to the applied electric field, the reversal mechanism involved pure switching. However, in cases where the polarization and electric field

are not parallel, the polarization reversal involved two mechanisms; polarization rotation and switching. Under the application of an electric field which is not parallel to the polarization vector, the crystal phase transforms and the polarization rotates before it actually switches. Demonstration of this dependence at single domain level is an experimental challenge. In this study, we have used the PFS technique to evidence the relation between the crystal orientation and coercive field for ferroelectric BaTiO₃ thin films. We show that PFS is a unique technique providing sufficient resolution to determine the polarization reversal mechanism of a single domain.

EXPERIMENTAL DETAILS

160 nm thick BaTiO₃ films were deposited on Pt/Ti/SiO₂/Si stack using pulsed laser deposition at a substrate temperature of 740 °C. Piezoresponse force spectra were acquired using a Park Systems XE 150 AFM. NSC-36 Ti/Pt b cantilever with a tip diameter of 80 nm was used to acquire the spectra. The alternating voltage applied to the tip had amplitude of 0.8 V and a frequency of 20 kHz. The spectra were taken by sweeping a DC bias from -8 V to +8 V (corresponding electric field from -600 kV/cm to +600 kV/cm) and vice versa. Stanford Research systems DSP lock-in amplifier, model SR830 was used to read the amplitude of the cantilever oscillation due to piezoelectric deformations. All measurements were taken at room temperature. Piezoresponse force microscopy (PFM) images were taken using NSC-36 Ti/Pt b cantilever in order to confirm the domain size. The polycrystalline nature of the film was confirmed through x-ray diffraction (XRD). Transmission electron microscopy (TEM) images were also taken to confirm the columnar growth of grains.

RESULTS and DISCUSSIONS

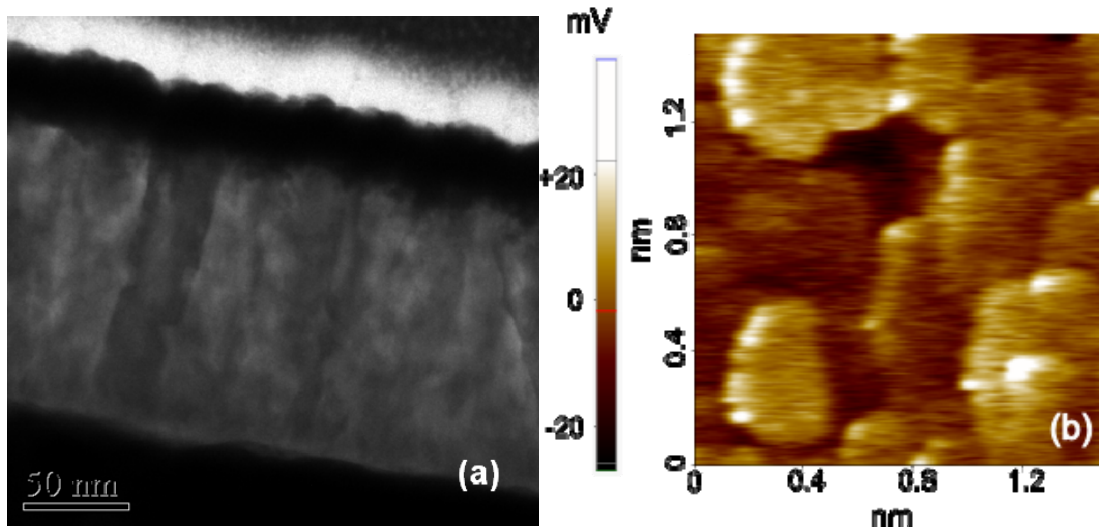


Figure 1. (a) Cross section bright field TEM image showing the columnar growth of BaTiO₃ grains. (b) PFM amplitude scan of 1.5 μm X 1.5 μm showing size of individual domains.

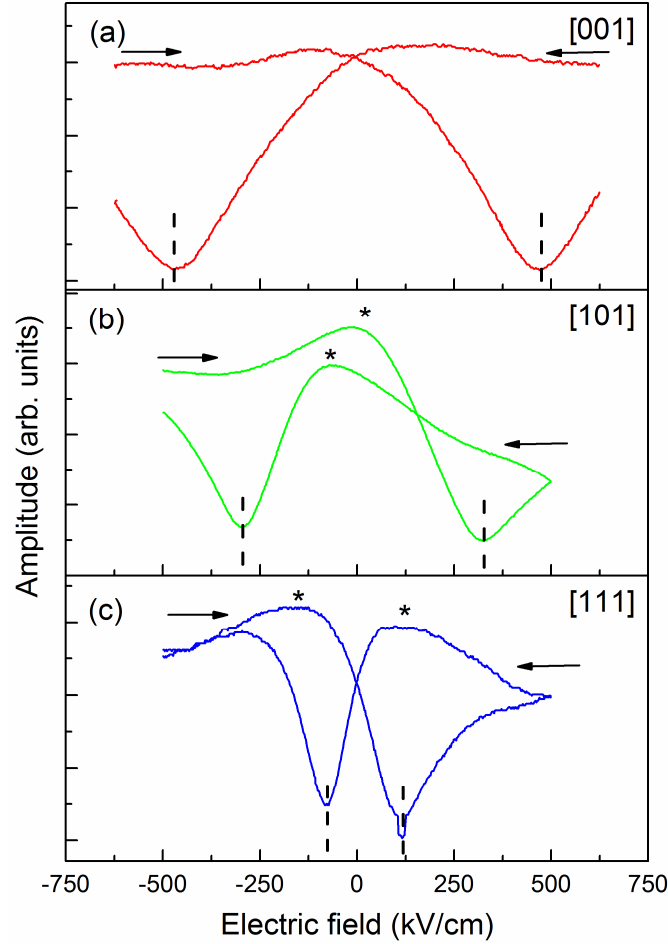


Figure 2. PFS spectra taken at three different domains. Arrows indicate the spectra for forward and reverse sweeping of the electric field. The coercive field (indicated by dotted lines) decreases as the grain orientation moves away from the out-of-plane axis. The domains are predicted as (a) [001], (b) [101] and (c) [111] as explained in the text.

Figure 1 (a) shows the TEM cross section bright field image of BaTiO₃. Columnar growth of domains would ensure that the piezoresponse force experienced by the AFM tip arises from a grain of single orientation stemming down to the bottom Pt electrode. The PFM scan (figure 1 (b)) shows that the domain sizes are much larger than the grain size and also the AFM tip size itself. Large domains with columnar grown grains would ensure that the PFS spectra taken on these domains would be mono-domain and the effects of nearby domains are minimized.

PFS spectra shown in figure 2 are at three different domains, which are deduced in the spectra by their shape of the piezoresponse when the electric field was swept from -600 kV/cm to $+600$ kV/cm. They all show differences in the shape of spectra and the switching field. PFS spectrum in figure 2 (a) shows minimum variation in the piezoresponse in comparison to those in figure 2 (b) and (c) as the electric field was decreased from its maximum value towards zero. This behavior shows the absence of enhanced piezoresponse and therefore the polarization rotation. The switching path in this domain exhibits the characteristics

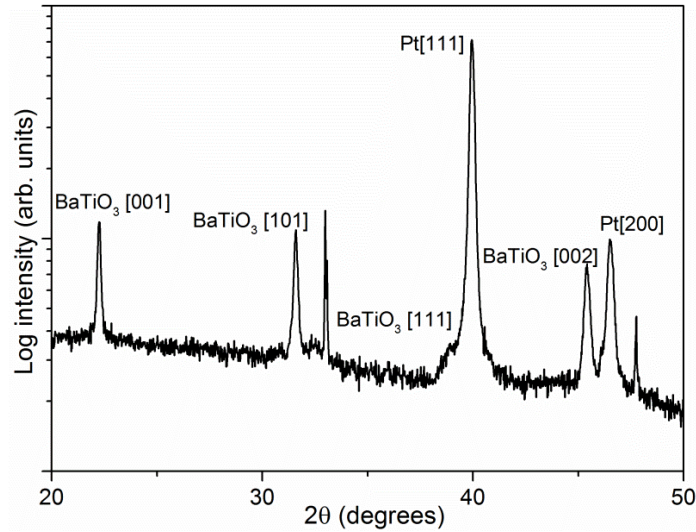


Figure 3. XRD spectra of BaTiO₃ on Pt showing [001], [101] and [111] preferred orientations of PLD grown BaTiO₃.

of pure switching mechanism occurring when the polarization is parallel to the electric field. In this case, as the electric field is swept from its maximum value towards zero, there is no field induced phase change and the piezoresponse remains same. Direct switching occurs at a coercive field when the electric field direction is opposite to the polarization direction. However, the domain in figure 2(a) shows a coercive field of 460 kV/cm which is higher than the switching fields shown by domains in figure 2(b) and (c). The absence of an enhanced-piezoresponse and the existence of a pure switching mechanism are predicted for [001] domains [6]. In contrast to the spectrum of the domain shown in figure 2(a), domains in (b) and (c) show enhanced piezoresponse (indicated by ‘*’ in figure 2 (b) and (c)). For figure 2 (b) and (c), the piezoresponse increases gradually as the applied field is reduced from the maximum values for both positive and negative sweeps. This is due to the enhanced piezoresponse and suggests the presence of a polarization rotation mechanism [5]. Polarization rotation is followed by switching at coercive fields with further sweeping of the electric field for both domains. Coercive field shown by the domains in figure 2 (b) and (c) are 330 kV/cm and 120 kV/cm respectively. These domains are deduced as [101] and [111] based on the field at which enhanced piezoresponse occurs. The correlation between the PFS spectra and crystal direction of these domains are explained below.

The direction of spontaneous polarization to the out-of-plane axis at zero electric field for tetragonal BaTiO₃ with [101] and [111] oriented grains are 45° and 54° respectively. In the case of BaTiO₃, the piezoresponse maxima due to an enhanced piezoresponse occur when the electric field makes an angle of 49° with the direction of polarization [7]. For the domain in figure 2 (b), these maxima are situated after zero electric field for both the forward sweep and for the reverse sweep. Hence, it could be deduced that at zero field polarization will be making an angle lower than 49° for this domain. This confirms that the domain in figure 2 (b) is [101] oriented. Similarly, for a [111] oriented grain the rotating polarization should pass through 49° before it reaches the zero field for the forward and reverse sweeps. As such, figure 2 (c) which shows piezoresponse maxima before the sweeping field approaches zero suggests that this particular domain is [111] oriented. The coercive field for the domain in figure 2(c) is lower than the

domains shown in figure 2(a) and (b). Indeed, the XRD spectra shown in figure 3 confirm the polycrystalline nature of the BTO film with [001], [101] and [111] preferred orientations, which is consistent with the PFS results.

It was shown that different crystal orientations show a different coercive field. The coercive field strength depends on the direction of crystal orientation with respect to the applied field. Figure 4 shows the switching field taken at five domains of each predicted orientations. When the polarization reversal is purely switching, which is the case for [001] domains, the coercive field is approximately 460 kV/cm. For [101] and [111] domains, in which the polarization reversal include polarization rotation and switching, the coercive fields are 330 kV/cm and 120 kV/cm respectively. The rotation of the polarization is found to help the domains to switch at lower fields compared to the scenario where the electric field and polarization direction are parallel.

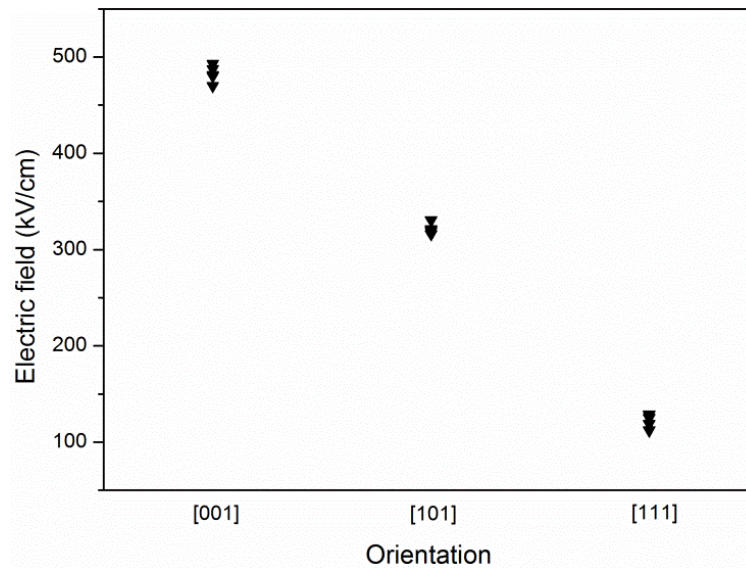


Figure 4. Variations in the switching field with variations in orientation based on five domains of each orientation for BaTiO₃.

CONCLUSIONS

PFS spectra were used to study the switching response of BaTiO₃ films at the resolution of individual domains. It was shown that spectra obtained from three different domains can be interpreted by the polarization reversal mechanism associated with the field induced phase transition as predicted by theoretical calculations. Based on this analysis, the PFS spectra were exploited to predict the crystal orientation of the domains, which were confirmed by XRD measurements. It was concluded that PFS provides a unique understanding of the relation between crystallographic orientation and switching mechanism in ferroelectric materials. PFS will be a valuable technique in characterization of future ferroelectric devices. A key outcome of the analysis being that the switching fields can be reduced by careful design of the film orientation, a critical factor in low power nano-ferroelectric devices.

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